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Comment on acp-2022-839

Anonymous Referee #1

Referee comment on "Sulfate formation via aerosol-phase SO₂ oxidation by model biomass burning photosensitizers: 3,4-dimethoxybenzaldehyde, vanillin and syringaldehyde using single-particle mixing-state analysis" by Liyuan Zhou et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-839-RC1>, 2023

Zhou et al. describe a series of laboratory flow-tube experiments analyzing sulfate formation via heterogeneous reaction of SO₂ and several types of photo-active organic particles. The results are interesting, demonstrate the utility of a novel analytical method (single-particle aerosol mass spectrometry) for observing particle-phase sulfate formation, and add to the rapidly growing body of works exploring atmospheric sulfate formation. I believe this paper merits publication in ACP after several major and minor comments are addressed, potentially involving additional experimentation. My comments are outlined below.

Major comments

I believe the authors need to more clearly highlight the apparent role of RH in these experiments and to more thoroughly explore the role that RH plays in the observed reactions. At line 221 the authors discuss that vanillin-coated particles produced substantially less sulfate at 20% RH relative to the 80% RH used in other experiments. RH therefore seems to be an important factor in affecting organic photosensitizer-initiated sulfate formation, but RH isn't mentioned as a factor in the abstract or the experimental description in the introduction. More thoroughly investigating the role that variable RH has on photosensitizer-initiated SO₂ oxidation would be very important to better understanding the significance of this pathway in ambient environments. Additionally, at line 158 the authors discuss potential SO₂ oxidants and note the possibility for oxidants that form from H₂O; does the apparent RH dependence point to H₂O as a secondary oxidant source following initial photo-excitation?

I have several questions about sulfate signal variability, mass spectral variability inherent to the SPAMS, and particle size.

- Line 110, section 2.2: how much variability are there in SPAMS spectra? E.g., how much variability in absolute peak area would be expected for monodisperse sulfate particles? What is the expected detection efficiency of the SPAMS for the observed size ranges of particles? Is it possible that any of the presented results are biased from low number statistics due to low particle detection efficiency and/or low numbers of particles? Does particle-phase water have any effect on desorption/ionization and RPAs/APAs? Even if some of these aspects of the SPAMS have been discussed in more detail previously some discussion here is necessary to fully understand and evaluate the presented results.

- There seems to be a lot of spread in the sulfate RPAs within the experiments (Line 146/Figure 2). Do the authors have a theory for this spread? Is SO₂ oxidation less efficient on some particles? Is there substantial spread in flow tube residence time? Is this just due to particle-to-particle variation in SPAMS ionization?
- On lines 172-174 the authors discuss an apparent size component to the efficiency of sulfate formation. Figure S4 clearly shows that the SPAMS sizing effectively captures the expected size distribution of the PSLs, but what size range do organic-coated particles span before sulfate formation begins? To put another way, how uniform is the population size distribution after becoming coated in organics? Do these results suggest that sulfate formation occurred unevenly across the particle population? Are there any instrumental factors that may influence the apparent size-dependent sulfate production efficiency? E.g., is it possible that larger particles are only partially ionized by the SPAMS and this skews the observed RPAs?
- At lines 209-211 the authors discuss the difficulties in using absolute peak areas to draw conclusions about sulfate signal. Are there circumstances where it would be feasible to translate the absolute peak area to some mass (or mass range) of sulfate and therefore be more quantitative about the amount of sulfate present in a particle? Would this be possible after observing APAs of size-selected sulfate particles and taking into account particle sizes measured by the SPAMS? Alternatively, is there a way to be reasonably quantitative about sulfate production rate from the studied photosensitizers, based on measurements like the amount of depleted SO₂ and particle surface area?

The authors note on lines 174-176 that the sulfate formation efficiency follows a similar trend as SOA formation from reaction between the three photosensitizers and syringol. What did the authors of the previous works attribute the difference in SOA production to? Would this be reasonable within the current system? Are there any other reasonable parameters that would influence the efficacy of SO₂ oxidation by these photosensitizers? E.g., absorption spectra, quenching efficiency, particle phase state or physical attributes.

Minor comments

General: I suggest adding subsections to the "Results and Discussion" to more clearly organize the different materials in this section, as some of the transitions within and between paragraphs are abrupt.

Line 58: what properties make vanillin a typical aromatic carbonyl sensitizer? Or is it just a photosensitizer that's often used in studies?

Lines 85-86: is the estimated organic coating thickness shown anywhere?

Line 151: what is the presence of (minor) sulfate under dark conditions attributed to?

Line 155: are any sulfite (SO₃) signals observed in the mass spectra? It doesn't appear so based on Figure 1 but it's a little difficult to tell. Would sulfite signals be expected to be visible while examining heterogeneous SO₂ oxidation?

Line 179: can the O₂-free environment influence any aspect of the ionization process?

Line 181: although the absolute changes in RPA are smaller for syringaldehyde particles, is the relative change similar to that for vanillin and DMB? Additionally, do the results in N₂ imply that direct 3C* oxidation of SO₂ can occur but is slower than pathways with O₂?

Line 186: specify what type of system Wang et al. (2020) was exploring.

Lines 188-189: have similar variations in 3C* reactions rates from different sources towards the same analyte been observed previously?

Line 193: can the decrease in organic ion RPA also be consistent with ion scavenging by newly produced sulfate?

Line 195: the location of the material following "Note..." seems odd and incongruous with the rest of the paragraph.

Lines 195-199: the authors seem to be implying that they do not expect the organic-coated PSLs to undergo substantial growth at the RH values used. If this is correct, please state so directly. Any other statements the authors intend to make here on particle physical characteristics should be clearly stated.

Line 203: to clarify, are the vanillin-coated particles here still PSLs?

Line 205: would pH and the identity of the NO₃⁻ counterion (e.g., H⁺, NH₄⁺) potentially influence SO₂ oxidation?

Line 210: is there any possibility for the different photosensitizers/organic particle matrices to lead to different sulfate ionization efficiencies and RPAs?

Line 214: it's not clear that the KNO₃ particles are deliquesced. Freney al. (2009) observed continuous growth with increasing RH for KNO₃ particles and a deliquescence RH of 90% for dried particles (in line with prior works cited in Freney et al.). Therefore, I don't believe the direct comparison to the sulfate formation in aqueous droplets used in Gen et al. (2019) is valid, and this comparison and discussion of photosensitizer vs nitrate SO₂ oxidation should be caveated with this information.

Line 224: is there a reason to suspect that oxalic acid/KNO₃ mixtures might affect SO₂ oxidation differently than pure KNO₃ particles?

Line 238-239: "qualitatively more efficient" under the studied conditions: wet aerosols at 80% RH.

Line 250: are photosensitizers emitted or formed in non-BB environments, for example urban environments where multifunctional aromatics are common emissions and high NO_x levels are common?